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DIFFUSION RATE OF Ca^{2+} ION IN THE MICROVOLUME OF CLINKER GRAIN

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The diffusion rate of calcium ion in multicomponent systems varies as a function of the composition of the mutually diffusing systems, properties of oxide-salt melts, and sintering temperature and time. In the reaction of clinker granule microvolumes of different composition, silicate formation is activated with an increase in the mobility of the Ca^{2+} ion, which increases by 3 – 40 times as a function of the content of salt systems when liquating zones of halide-sulfate appear in the melt.

In firing silicate materials, the difference in the rates of dissolution of CaO and $2CaO \cdot SiO_2$ (C_2S) and the mobilities of silica anions and calcium ions causes regions of different composition to be formed in the melt. As a function of the composition of these regions, the limiting stage of the silicate formation process can change. In zones with a high concentration of Ca^{2+}, Na^+, and K^+ ions, belite (C_2S) intensively corrodes and synthesis of $3CaO \cdot SiO_2$ (C_3S) is determined by the rate of dissolution of calcium oxide. In belite regions, formation of C_3S is limited by the diffusion rate of Ca^{2+} from more highly basic regions of the melt to C_3S crystal nuclei and the rate of dissolution of C_2S [1, 2]. The kinetics of the reaction of calcium oxide with the belite region is limited by diffusion of calcium ions. However, the diffusion rate of the ions varies in different zones of the melt and is determined by their composition.

Melt zones rich in Ca^{2+} are formed between grains of CaO – C_2S, CaO – C_3S, and CaO – C_2S – C_3S, where C_3S crystals originate. Zonally positioned melts characterized by concentration gradients and different acid-base properties react on contact on the interface with the ions, approaching the equilibrium composition. In large volumes of melt, convection causes neutralization of the composition, but transfer of matter in fine capillaries and films only takes place due to diffusion. Preservation of volumes of melt in clinker grains of different composition and the presence of liquation liquids causes separation of solid phases in equilibrium with these liquids.

The rate of alite formation (synthesis of C_3S) was estimated with the values of the effective calcium ion diffusion coefficients D_{Ca} in local volumes (CaO + melt (M)) – (C_2S + M); (CaO + C_2S + M) – (C_2S + M) and (CaO + C_3S + M) – (C_2S + M). The model systems schematically illustrated in Fig. 1 were prepared and the compositions of mutually diffusing systems are reported in Table 1. Calcium oxide labeled with β-active Ca^{45} isotope was incorporated in the CaO + M, CaO + C_2S + M, and CaO + C_3S + M systems.

After firing at 1400 and 1450°C with different isothermal holding, the distribution of CaO in the depth of the sample was determined and the value of the effective diffusion coefficient was calculated with Fick's equation for diffusion in a semi-infinite space.

The change in the Ca^{45} content in the depths of the sample was exponential for all systems (Fig. 2*a*), which was confirmed by the linearity of function $\log I - a$, where a is the sample thickness (Fig. 2*b*). D_{Ca} decreased with an increase in the duration of isothermal sintering due to densification of the structure of the clinker (Table 2).

The highest value of D_{Ca} was observed for the (CaO + M) – (C_2S + M) system, which was due to the absence of any chemical reaction in the CaO + M system. In the CaO + C_2S + M system, C_3S is formed in the system itself parallelly with diffusion of Ca^{2+} ions from the disk of

TABLE 1

System	Mass content, %*		
	CaO	C_2S	C_3S
CaO + M	70	–	–
CaO + C_2S + M	40	30	–
CaO + C_3S + M	40	–	30
C_2S + M	–	70	–

* In all cases, the melt content was 30%.

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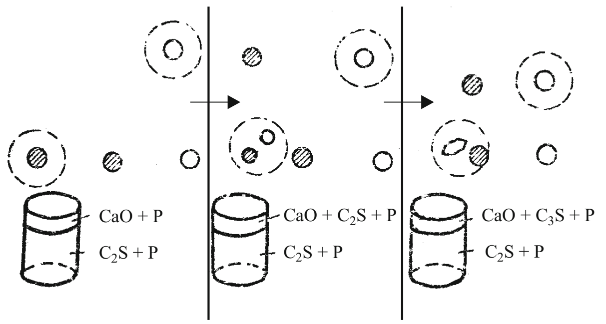

Fig. 1. Schematic illustration of model systems: ●) CaO; ○) C_2S; ⬡) C_3S.

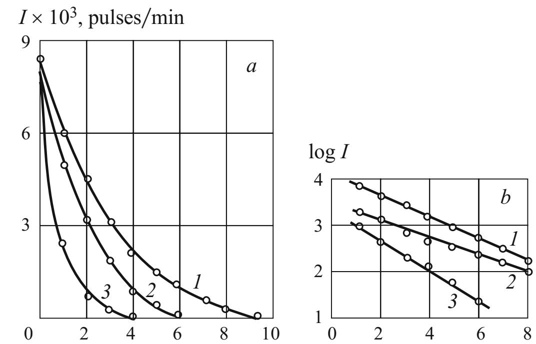

Fig. 2. Change in the radiation intensity I over the sample thickness: *a*) in the (CaO + M) – (C_2S + M) system at 1400°C and duration of 10 min (*1*), 20 min (*2*), and 30 min (*3*); *b*) at 1400°C and duration of of 10 min for the systems: *1*) (CaO + M) – (C_2S + M); *2*) (CaO + C_3S + M) – (C_2S + M); *3*) (CaO + C_2S + M) – (C_2S + M).

CaO + C_2S + M in C_2S + M, and this decreases the depth of penetration of Ca^{2+} through the phase interface, thus decreasing the value of the calculated D_{Ca}. The effective diffusion coefficient of the calcium ion in these systems is almost two times less than the D_{Ca} in the clinker liquid phase, primarily due to the occurrence of silicate formation reactions and the tortuosity of the diffusion path and the effect of the surface of solids in diffusion in fine capillaries [3, 4].

Comparing the results obtained with the published data on the diffusion rate of CaO in clinker [5], we find that the agreement of the results is satisfactory.

In modification of clinker liquid phase with different elements, the viscosity of the melt changes, which causes a change in D_{Ca} and consequently the rate of propagation of the zone of C_3S. The effect of the properties of the melt on the calcium ion diffusion rate was investigated in the (CaO + M) – (C_2S + M) model system. The melt was modified with two complexes of additives — $CaF_2 + CaSO_4$ (in the molar ratio of 50% CaF_2, 50% $CaSO_4$) and $R_2O + MgO + SO_3$ (where $R_2O : MgO : SO_3$ = 1 : 8 : 11; $R^+ = K^+, Na^+$). Increasing the content of trace elements in the melt increased the effective diffusion coefficient (Table 3).

D_{Ca} increased especially effectiveness at a mass content of 3 – 5% modifiers in the melt. In incorporation of 3% ($CaF_2 + CaSO_4$) and ($R_2O + MgO + SO_3$), the effective diffusion coefficient increased from 2.50×10^{-9} to 21.30×10^{-9} and 4.46×10^{-9} m²/sec, respectively, obeying the Stokes – Einstein law. The 3 – 5% content of complex modifiers corresponds to the region of additive concentrations that cause separation of clinker melt. In the presence of the R_2O + MgO + SO_3 complex, liquation events were detected at a 3% content, while in the presence of $CaF_2 + CaSO_4$, it was detected at a content of more than 1% [6, 7]. The results of determining D_{Ca} (see Table 3) are in good agreement with the liquating power of the melt. As a consequence, the appearance of liquating phases in clinker liquid that cause an important decrease in the viscosity increases the calcium ion diffusion rate.

The thickness of the alite layer at the sites of contact of local sections of CaO + M and C_2S + M increased with an increase in the sintering time (Fig. 3). If alite formation is limited by diffusion, then the width of the alite layer X will be proportional to $\sqrt{\tau}$ [8]. Mathematical processing of the results obtained showed that the kinetics of the increase in the C_3S zone is expressed by a parabolic dependence:

$$X = \frac{K}{\eta}\sqrt{\tau},$$

where X is the width of the C_3S zone, m, to time τ, sec; K is a constant dependent on the properties of the solid phases; η is the viscosity of the clinker liquid phase, Pa · sec.

Similar dependences are characteristics of the systems (CaO + C_2S + M) – (C_2S + M) and (CaO + C_3S + M) – (C_2S + M). The presence of elements that decrease η in the melt (K_2O, Na_2O, for example) slows the growth of the C_3S layer around the CaO grains. In the low-viscosity clinker liquid phase (for example, in the presence of SO_3, F^-, $R_2O + MgO + SO_3$, etc.), alite formation is accelerated, which intensifies and increases X (see Fig. 3). The increase in the thickness of the alite layer

TABLE 2

Firing regime		Effective calcium ion diffusion coefficient $D \times 10^9$, m²/sec in system			
temperature, °C	duration, min	(CaO + M) – (C_2S + M)	(CaO + C_2S + M) – (C_2S + M)	(CaO + C_3S + M) – (C_2S + M)	M [2]
1400	10	1.41 ± 0.02	0.53 ± 0.01	1.39 ± 0.01	–
	20	1.30 ± 0.01	0.44 ± 0.02	1.23 ± 0.01	
	30	1.20 ± 0.02	0.36 ± 0.01	1.12 ± 0.01	
1450	10	2.82 ± 0.02	2.41 ± 0.01	2.79 ± 0.02	5.31
	20	2.56 ± 0.01	2.01 ± 0.02	2.43 ± 0.02	
	30	2.36 ± 0.02	1.75 ± 0.01	2.19 ± 0.03	

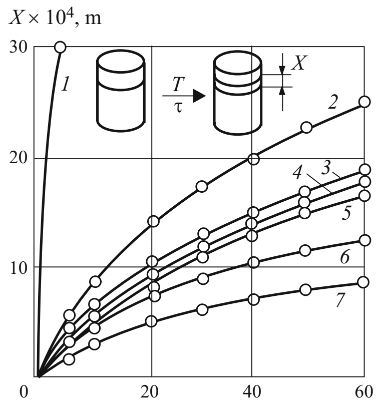

Fig. 3. Effect of the sintering time on the change in the thickness of the alite layer X in the $(CaO + M) - (C_2S + M)$ system in the presence of: *1*) $CaF_2 + CaSO_4$; *2*) F^-; *3*) $R_2O + MgO + SO_3$; *4*) SO_3; *5*) MgO; *6*) initial melt; *7*) R_2O ($Na_2O + K_2O$).

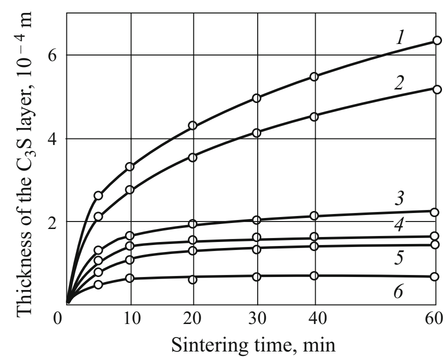

Fig. 4. Kinetics of the change in the thickness of the C_3S layer around the regions of calcium oxide with a size of 0.5×10^{-4} (*2*, *5*, *6*) and 1.0×10^{-4} (*1*, *3*, *4*): *1*, *2*, *3*, *5*) calculated values; *4*, *6*) experimental data.

in time can arbitrarily be separated into two stages: under 15 – 20 min of sintering, an intensive increase in X with the time is characteristic. The layer of C_3S formed subsequently inhibits diffusion of Ca^{2+} and SiO_4^{4-} ions, and the rate of the increase in X is slowed.

The belite regions are usually located around the calcium oxide regions during sintering of clinkers. A layer of C_3S is formed on the $CaO - C_2S$ boundary. The change in the concentration of calcium oxide C in this alite layer is only a function of distance r from the center of the CaO grain to the boundary with C_2S. The concentration $C(r)$ can be found from solving Fick's equation, which is as follows from the case of spherical symmetry and in spherical coordinates:

$$\frac{dC}{d\tau} = D\left(\frac{d^2C}{dr^2} + \frac{2}{r}\frac{dC}{dr}\right),$$

where D is the diffusion coefficient.

The kinetics of the reaction is described by the equation:

$$1 + \frac{2}{3}\alpha - (1 + \alpha)^{2/3} = K\tau,$$

where α is the degree of bonding of CaO with C_2S in C_3S.

The rate of alite formation is usually estimated with the amount of unassimilated calcium oxide. However, studying the kinetics of the change in the alite layer is of some interest. There are almost no such studies in the literature.

Based on geometric considerations, the increase in the thickness of the alite layer around the spherical region of CaO can be described by the equation:

$$X = \sqrt[3]{3r_0^2 K \frac{\sqrt{\tau}}{\eta} + r_0^3} - r_0 .$$

The results of calculating the thickness of the C_3S layer show an important difference in the values obtained (Fig. 4). This is because the amount of C_2S that totally reacts with a CaO region of a certain size is not always taken into account. The experimental results (see Fig. 4) show that X increases intensively up to a certain sintering time τ_0. Increasing the sintering time $\tau > \tau_0$ almost does not increase X. As a consequence, there is a limiting value for the alite layer thickness for each size of the calcium oxide region.

The melt formed in belite regions migrates into the CaO region due to surface tension forces, filling microcapillaries and impregnating aggregates of particles. In view of this and with respect to the model examined, a calcium oxide region r_0 in size can react with a belite region V_{C_2S} in size:

$$V_{C_2S} = \frac{4(1-\alpha_{CaO})M_{C_2S}\rho_{CaO}}{3(1-\alpha_{C_2S})M_{CaO}\rho_{C_2S}}\pi r_0^3, \tag{1}$$

where α_{CaO} and α_{C_2S} are the amount of melt in the CaO and C_2S regions; M_{CaO} and M_{C_2S} are the molar mass of CaO and C_2S; ρ_{CaO} and ρ_{C_2S} are the density of CaO and C_2S.

TABLE 3

Melt modifier, wt.%	Properties of melt		
	viscosity, Pa · sec	surface tension, N/m	$D_{Ca} \times 10^9$, m^2/sec
–	0.160	0.580	2.50
$1.5(CaF_2 + CaSO_4)$	0.042	0.472	9.10
$3.0(CaF_2 + CaSO_4)$	0.017	0.458	21.30
$5.0(CaF_2 + CaSO_4)$	0.004	0.426	93.60
$1.5(R_2O + MgO + SO_3)$	0.117	0.450	3.08
$3.0(R_2O + MgO + SO_3)$	0.080	0.415	4.46
$5.0(R_2O + MgO + SO_3)$	0.007	0.388	48.90

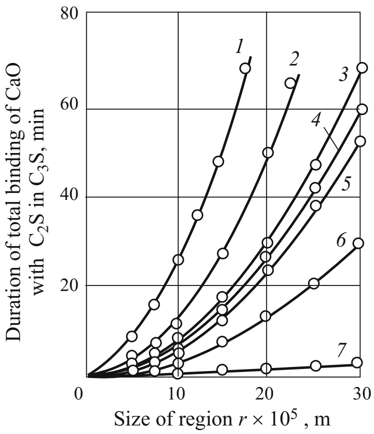

Fig. 5. Effect of the average calcium oxide particle size on the duration of alite formation in melts containing 3 wt.% modifier: *1*) R_2O ($Na_2O + K_2O$); *2*) initial melt; *3*) MgO; *4*) SO_3; *5*) R_2O + MgO + SO_3; *6*) F^-; *7*) $CaF_2 + CaSO_4$.

In view of Eq. (1), the thickness of the diffusion layer X of the reaction product is equal to:

$$X = r_0 \sqrt[3]{\frac{(1-\alpha_{CaO}) M_{C_2S} \rho_{CaO}}{(1-\alpha_{C_2S}) M_{CaO} \rho_{C_2S}} + 1}. \quad (2)$$

It follows from Eq. (2) that in total binding of CaO, the thickness of the C_3S layer will be greater than the region of the initial calcium oxide. Equation (2) allows estimating the thickness of the alite layer around the calcium oxide regions (grains) formed in using coarsely crystalline limestone. With respect to the model examined, the necessary sintering time for total binding of a calcium oxide region (grain) of size r_0 can be determined with Eq. (2) (Fig. 5):

$$\tau = K\eta^2 r_0 \left[\left(\sqrt[3]{\frac{(1-\alpha_{CaO}) M_{C_2S} \rho_{CaO}}{(1-\alpha_{C_2S}) M_{CaO} \rho_{C_2S}} + 1} + 1 \right)^3 - 1 \right]^2 . \quad (3)$$

At the beginning of the sintering zone of rotary furnaces, the dispersion of calcium oxide is equal to 35 – 60 μm. For this dispersion, the duration of total binding of CaO in C_3S, calculated with Eq. (3), will be 35 – 60 min, which is in good agreement with the real residence time of the material in the sintering and cooling zones of rotary furnaces. As a consequence, Eq. (3) can be used for estimating the clinker sintering time.

In modification of a clinker melt with different elements or their composites, its properties change, which causes a change in the rates of dissolution and crystallization of minerals. For this reason, when modifiers are added, the sintering time decreases. When 3 wt.% F^- is added, the time for assimilation of 40 μm CaO grains decreases from 52 to 14 min, while it decreases to 3 min in liquating oxide-salt fluorosulfate melt — 3% ($CaF_2 + CaSO_4$) (see Fig. 5). On the other hand, when the viscosity of the melt decreases from 0.16 to 0.04 Pa · sec, the size of the CaO region totally turning into alite in 20 min increases by 2 times.

The calcium ion diffusion rate in multicomponent systems thus varies as a function of the composition of the mutually diffusing systems, properties of the oxide-salt melts, and the sintering temperature and time. In the reaction of clinker granule microvolumes of different composition, silicate formation is activated with an increase in the mobility of the Ca^{2+} ion, which increases by 3 – 40 times as a function of the content of salt systems when liquating zones of halide-sulfate composition appear in the melt.

The characteristics obtained can be used for predicting the mechanism and kinetics of sintering of silicate materials that takes place with the participation of a liquid phase.

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